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Procedia Chemistry 7 (2012) 581 – 586

Procedia Chemistry

ATALANTE 2012
International Conference on Nuclear Chemistry for Sustainable Fuel Cycles

Simplified nuclear glasses structure behaviour under various irradiation conditions: a Raman spectroscopy study

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Abstract

The effects of the ^{244}Cm alpha decays, 1-3.5-7 MeV multi-energy gold ions irradiations and 74 MeV krypton ions irradiation) on the structure of a six oxide glass (SiO_2-B_2O_3-Na_2O-CaO-Al_2O_3-ZrO_2) are compared using Raman spectroscopy.
The results suggest that the effects on the glass properties induced by these three kind of irradiations are similar, revealing a depolymerisation of the silicate network and a decrease of the boron coordination number.

Nuclear glass ; irradiations ; displacements cascade ; Raman spectroscopy ; thermal quenching

1. Introduction

For many years, studies to assess the impact of the alpha decay accumulation on the confinement properties of nuclear glasses are performed by CEA. An approach combining studies on ^{244}Cm doped glasses [1], non-radioactive glasses irradiated with external ion beams [2,3] as well as atomistic simulations [4,5] led to describe the glass structure evolution mechanisms and their consequences on the glass properties. A model of local thermal quenching of ballistic disordering [4, 6] was recently proposed to explain the impact of nuclear interactions (displacement cascades) induced by alpha decays in glasses. In this model the recovering phase following the displacement cascade is interpreted as a quenching phase from the disordered state caused by the

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doi:10.1016/j.proche.2012.10.088

displacement cascade. This description is close to the one of the thermal spike model used to describe the ion tracks formation induced by swift heavy ions [7,8]. In this model, when the electronic stopping power of the incoming heavy ion overcomes a threshold, the electronic interactions induce, locally along the ion path, a melted state that is rapidly quenched forming an ion track.

The aim of the present study is to compare the effects of various irradiations conditions on the structure of a borosilicate glass. A 6 oxyde (SiO_2-B_2O_3-Na_2O-CaO-Al_2O_3-ZrO_2) glass (SIBCAZ) was doped with ^{244}Cm doped to evaluate the effects of alpha decays. Two non radioactive glasses were externally irradiated with 1, 3.5, 7 MeV multi-energy gold ions or 74 MeV krypton ions. The gold ions irradiations simulate the displacements cascades whereas the high energy krypton irradiations induce ion tracks.

2. Samples and Methods

2.1. Samples preparation

Table 1: Glass compositions in wt%.

Oxide	SiO_2	B_2O_3	Na_2O	CaO	Al_2O_3	ZrO_2	Cm_2O_3	PuO_2	total
SBNCAZ	56,18	17,33	12,17	4,98	6,06	3,28	-	-	100
SBNCAZ-Cm	55,32	17,07	12	5,01	6,03	3,26	1,02	0,29	100

The SBNCAZ glass was synthesized by melting oxides, carbonates and nitrates. The mixture was melted for 3 h at 1400 °C in a platinum-rhodium-yttrium crucible without stirring and casted in a graphite crucible. The glass was then annealed above the glass transition point (600 °C) from which it was cooled more slowly to release the residual stresses from the glass.

A SBNCAZ glass sample doped with 0.7wt % $^{244}Cm_2O_3$ (SBNCAZ-Cm) was synthesized in Atalante hot cells facility by melting oxides, carbonates and nitrates. The mixture was melted for 3 h at 1400 °C without stirring, then quenched to a temperature slightly above the glass transition point (600 °C), from which it was cooled more slowly to release the residual stresses from the glass. The cylindrical glass rod of 15 mm of diameter was cut into 1.5 mm thick disks.

Table 1 presents the chemical composition of the glasses.

The first Raman spectrum of the glass was recorded five months after its synthesis and the glass already accumulated an alpha decay dose of $3.75x10^{17}$ α/g at that time. To obtain the spectrum of the pristine glass, one glass disk was annealed at 600 °C during six hours and then slowly cooled. A Raman spectrum was recorded 14 days after the annealing which correspond to an alpha decay dose of $3.07x10^{16}$ α/g. The maximum alpha decay dose that was sustained by the SBNCAZ-CM glass is $3.2x10^{18}$ α/g.

Table 2: Irradiation conditions.

	Au (multi-energy)			^{244}Cm alpha disintegration		Kr
				Recoil nucleus	α particle	
Energie (MeV)	1	3.5	7	0.095	5	72
Fluence (ion/cm^2)	4.6×10^{13}	1.4×10^{14}	3.2×10^{14}	-	-	3.0×10^{13}
Dose (α/g)	-	-	-	3.2×10^{18}		-
E_{nucl} (KeV/cm^3) *		3.8×10^{21}		4.9×10^{20}	8×10^{19}	5.7×10^{18}
E_{elec} (KeV/cm^3) *		1.3×10^{22}		3.2×10^{20}	4×10^{22}	3.0×10^{21}

* from SRIM simulation [9], the secondary cascades are included in the calculated energies.

2.2. Irradiation conditions

The Table 2 sums up the various irradiation conditions.

2.2.1. Gold irradiations

1, 3.5 and 7 MeV Au ions are used to study the effects of both electronic and nuclear (ballistic) interactions on the SBNCAZ glass. Previous studies on complex borosilicate glass with these irradiation conditions [1,2] showed that the nuclear interactions (displacement cascades) are the main source of structural modifications of the glass. The samples were irradiated at the ARAMIS accelerator at CSNSM in Orsay. The energies of the incoming ions were chosen to maximize the irradiated depth (~1.8 µm) which is compatible with the depth resolution of the Raman microspectrometer device and to obtain a homogeneous energy deposition by nuclear interaction is this range (Figure 1).

2.2.2. Krypton irradiations

To study the effect of ions tracks formation on the SBNCAZ glass, some samples were irradiated with 74 MeV Kr ions at the IRRSUD accelerator at GANIL in Caen. The maximum electronic stopping power is around 10 keV.nm^{-1} (Figure 1). The appearance threshold of ion tracks is not yet known in the SBNCAZ glass, but such a stopping power allows their formation in most of the insulators [10] and in particular in silica glass. The irradiated depth is around 12 µm.

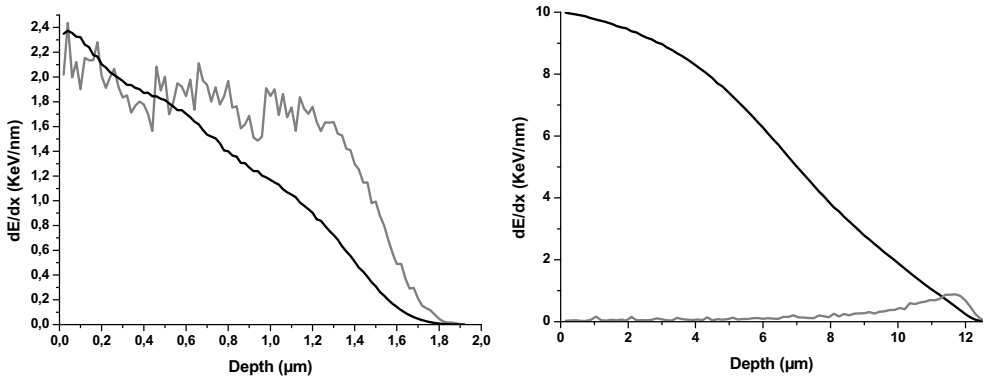

Figure 1: Electronic (black) and nuclear (grey) stopping powers of the incoming ion versus the irradiated depth for 1-3-6.75 MeV gold ions (left) et 74 MeV krypton ions irradiations in the SBNCAZ glass (SRIM2008 [9] simulations).

2.3. Raman spectroscopy

The Raman spectra have been recorded at room temperature on a DILOR Labram microspectrometer with a 1800 grooves per mm grating with a spectral resolution around 1.6 cm^{-1}. The laser (532 nm) was focused on the sample thought a 100 x objective delivering 9 mW on the sample. For the krypton and gold ions irradiated SBNCAZ glasses, the samples were embedded in a resin and the spectra recorded close to the resin. The laser power was then kept below 9 mW to avoid the alteration of the resin. The signal was collected through a 100 µm open pinhole and a 200 µm open slit on a Peltier-cooled charge-coupled device (CCD).

To record the spectra of SBNCAZ-Cm glass, the microspectrometer was coupled with optical fibers to an optical microscope situated in a hot cell. The signal was collected through a 100 x objective delivering 17 mW on the sample.

3. Results

3.1. SBNCAZ-Cm glass

Raman spectra of the SBNCAZ-Cm glass were recorded at different accumulated doses (

Figure 2). The strong signal of the Cm3+ luminescence interferes with the Raman spectra above 1200 cm^{-1}, avoiding the interpretation of the borate band around 1450 cm^{-1}.

Three main modifications of the SBNCAZ Raman spectrum with the alpha decay dose can be observed. There is first a shift of the band at 490 cm^{-1} towards the higher wave numbers. The band at 490 cm^{-1} is usually attributed to Si-O-Si bonds vibration and the shift towards the higher wave numbers attributed to a decrease of the Si-O-Si mean angle [11,12,13].

The second change in the Raman spectrum is the intensity increase with the dose of a band at 605 cm^{-1}. This could reflect the emergence of the D2 band that corresponds to the Si-O-Si bonds vibration in three-membered [SiO_4] rings [11,12].

Finally, there is a strong increase with the alpha decay dose of the 1070 cm^{-1} band intensity. This band is usually attributed in silicate [14] and borosilicate [15,16] glasses to the stretching vibration of the Si-O bonds in [SiO_4] tetrahedron with three bridging oxygen atoms (Q_3 band).

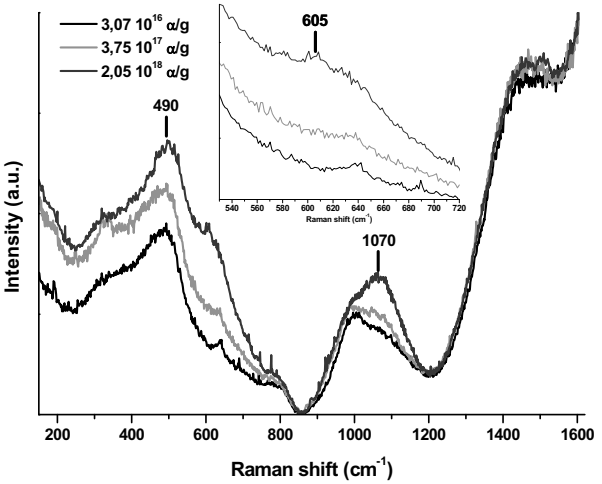

Figure 2: Raman spectra of the SBNCAZ-Cm glass that accumulated 3.07 10^{16} α/g (black), 3.75 10^{17} α/g (soft grey) and 2.05 10^{18} α/g (grey). The 530-720 cm^{-1} area is presented in a close-up.

3.2. SBNCAZ externally irradiated glasses

The spectra of the gold and krypton irradiated SBNCAZ glasses are presented in figure 3. A shift of the band at 490 cm^{-1} towards the higher wave numbers, an intensity increase of the D2 (605 cm^{-1}) and Q_3 (1070 cm^{-1}) bands are also observed. But these variations are coupled with four other variations that could not be observed on the SBNCAZ-Cm glass because of the baseline variations and Cm^{3+} luminescence.

First, there is an intensity decrease of a band situated at 770 cm^{-1}. This band is attributed to a ring breathing mode of 6-membered boron rings containing several BO_4 groups [17].

There is also a decrease of the Raman signal intensity near 1000 cm^{-1}. This band could be attributed to Q_2 species, i.e. [SiO_4] tetrahedron with two non bridging oxygen atoms. But for this glass composition ^{29}Si NMR

experiment did not show significant Q_2 species. We prefer to attribute this band to the vibration of Q_4(B, Zr) groups [14,15,16] that correspond to [SiO_4] tetrahedron with four bridging oxygen atoms, in which at least one of the bridging oxygen atom is bonded to a zirconium or a boron atom.

An evolution of the band between 1300 and 1600cm^{-1} can also be observed and shows an intensity increase of the band around 1480 cm^{-1} corresponding to the elongation vibration of the B-O-B bonds when [BO_3] units are linked to [BO_3] units and an intensity decrease of the band at 1410 cm^{-1} corresponding to the elongation vibration of the B-O-B bonds when [BO_3] units are linked to [BO_4]$^-$ units. This evolution seems to be coherent with the decrease of the band at 770 cm^{-1}.

Finally, there is the emergence of a small band around 1545 cm^{-1}, characteristic of the stretching vibration of molecular O_2 dissolved in the glass [18]that can appear due to alkaline migration under irradiation [19].

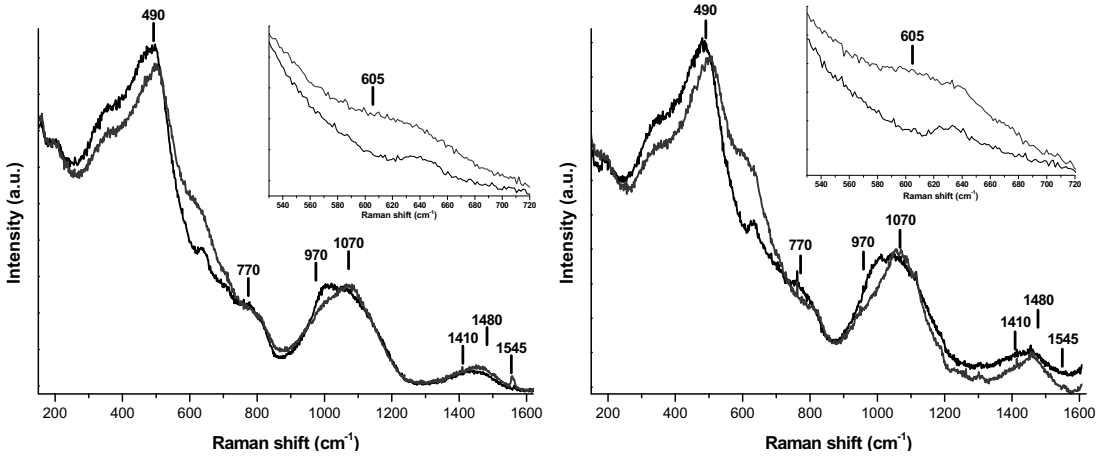

Figure 3: Raman spectra of the SBNCAZ before (black) and after (grey) 1, 3.5, 7 MeV Au ions (left) and 74 MeV Kr ions (right) irradiations. The 530-720 cm-1 area is presented in a close-up.

4. Discussion and conclusion

The variations of the SBNCAZ Raman spectra are similar for the three kinds of irradiations.

The shift of the vibration band situated at 490 cm-1 correspond to a decrease of the Si-O-Si angle that could be characteristic of a depolymerisation of the silica network [3,20,21], which would be consistent with the decrease of the Q_4[B, Zr] bands intensity and the increase of the Q_3 one.

The boron environment is also affected with the decrease of the band at 770cm^{-1} (6-membered boron rings containing several BO_4 groups) and the decrease of the 1410 cm^{-1} band intensity ([BO_3] – [BO_4]$^-$ vibrations) coupled with the increase of the 1480 cm^{-1} band intensity ([BO_3] – [BO_3] vibrations).

These results suggest a partial conversion of [BO_4]$^-$ to [BO_3] and a depolymerisation of the silicate network ($Q_n \rightarrow Q_{n-1}$ + 1 non bridging oxygen).

These local order variations and the emergence of D2 band that corresponds to three-membered [SiO_4] rings are consistent with the effects of displacements cascades accumulation in simple borosilicate glasses [3,22] that frozen a higher fictive temperature state that the un-irradiated one.

These results suggest that alpha decays, displacement cascades and ion tracks have the same impact on the glass structure. These irradiations all create a locally disordered state that is rapidly quenched. Because the locally disorder state associated to these three type of irradiations are certainly different, these results suggest that the final irradiated state is mainly controlled by the relaxation step following the disordering.

These interpretations need to be confirmed by coupling NMR studies on the three types of irradiated glasses.

Acknowledgments

The authors are grateful to the JANUS at CSNSM (Orsay) and IRSSUD at GANIL (Caen) staff for their technical and scientific support on ion irradiations. Sincere thanks are extended to the Atalante staff for their technical support. This study was also carried out under a research program funded by CEA and AREVA-NC.

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